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| 13. ABSTRACT (Maximum 200 words) Cyclopentadienyl rings with substituents that interlock with those of a second ring form "encapsulated" metallocenes ((C ₅ R ₅) ₂ M) with the alkaline-earth metals (Ca, Sr, Ba). These metallocenes are conveniently manipulated, volatile, hydrocarbon-soluble sources of the metal cations, which make the compounds attractive as precursors to metal oxides and ceramics. The physical properties of the metallocenes are highly sensitive to the degree of encapsulation and to the geometry of the encapsulating ligands; more flexible rings reduce the ability of complexes to pack into lattices, and oils and waxes will be formed. Other main-group metals (Sn, Pb) and lanthanide elements (Sm) can be encapsulated with the same ligands used for the alkaline-earths. Under the proper conditions, a ring can be displaced from an encapsulated metallocene, exposing the metal center and activating the complex. Disproportionation of the resulting mono(ring) complexes (C ₅ R ₅)M[E] into symmetrical (C ₅ R ₅) ₂ M and M[E] ₂ species can be blocked. "Ligand synergism" in mono(ring) complexes can enhance their chemical and thermal stabilities relative to those of the parent symmetrical species. | | | |
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Encapsulated Alkaline-earth Organometallics as Controlled Sources of Calcium, Strontium, and Barium Ions

FINAL REPORT

Timothy P. Hanusa

June 28, 1994

U.S. Army Research Office

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Encapsulated Alkaline-earth Organometallics as Controlled Sources of Calcium, Strontium, and Barium Ions

I. Statement of Problem

Many advanced ceramics with unique mechanical, thermal, optical, and electronic properties incorporate the electropositive alkaline-earth metals (Ca, Sr, Ba) or the lanthanide elements (La–Lu).¹ Fabrication methods such as chemical vapor deposition (CVD) and sol-gel techniques place exceptional demands on precursor materials, which must possess appropriate, and sometimes conflicting, combinations of volatility, thermal stability, and chemical reactivity. Simple alkoxides (e.g., methoxides, ethoxides) or organometallic compounds (e.g., methyls, *n*-butyls, cyclopentadienyls) that might be suitable as precursors to oxides of small metals do not work well with the large alkaline-earth and lanthanide elements. The ligands do not provide adequate steric saturation for the metal centers,² and the compounds are often nonmolecular and have relatively high sublimation temperatures. Attempts to improve their volatility have focused on suppressing their oligomerization, either with the use of sterically bulky ligands, or by the addition of various solvents, gases or excess free ligand.^{3–6} Considering the difficulties that have been encountered with improving the volatilities of these materials, it is not surprising that little attention has been given to modifying other properties, such as melting or boiling points. Because of their constant surface area, liquid alkaline-earth oxide precursors could be expected to have more reproducible transport properties than would volatile solids.⁷

The focus of this research was to explore ways in which the alkaline-earth metals calcium, strontium, and barium could be incorporated into conveniently manipulated, volatile, hydrocarbon-soluble sources of the metal cations that could serve themselves as, or be used as models for, precursors to ceramics and other specialized metal oxides. The primary emphasis was on the use of metallocenes ($(C_5R_5)_2M$) containing substituents that interlock with those of a second ring, thereby “encapsulating” the metal center. It was expected that these metallocenes could be tailored to provide high volatility and selective

reactivity toward Lewis bases. Thus the research was designed to (1) increase the number and variety of known "encapsulated" organoalkaline-earth metallocenes, attempting to control physical properties such as volatility and melting point; and (2) use them as reagents to introduce heavy alkaline-earth cations into reactions under controlled conditions.

II. Key Findings

A. Background

1. Metallocenes

Alkaline-earth (Ae) metallocenes are readily prepared by metathesis of an alkali metal cyclopentadienide and an alkaline-earth halide (eq 1).⁸



A wide range of derivatives is accessible with this method, including those with sterically demanding groups such as $[(\text{Me}_3\text{Si})_2\text{C}_5\text{H}_3]^-$, C_5Me_5^- , and $\text{C}_8\text{H}_8^{2-}$. Among the best studies are the decamethylmetallocenes $(\text{C}_5\text{Me}_5)_2\text{Ae}$, which are hydrocarbon-soluble Lewis acids, and form adducts with a variety of Lewis bases, including ethers, aromatic amines, metal carbonyls and unsaturated hydrocarbons.^{9,10}

By using cyclopentadienyl rings with isopropyl substituents, such as $[(i\text{-Pr})_4\text{C}_5\text{H}]^-$ ¹¹ "encapsulated" metallocenes can be produced that display considerable selectivity toward Lewis bases. The complex $(\text{Cp}^{4i})_2\text{Ca}$ ($\text{Cp}^{4i} = (i\text{-Pr})_4\text{C}_5\text{H}$), for example, does not form adducts with neutral donors such as ethers and aromatic amines, and in stark contrast to the extreme air-sensitivity of $(\text{C}_5\text{Me}_5)_2\text{Ca}$, $(\text{Cp}^{4i})_2\text{Ca}$ can be handled for several minutes in dry air without decomposition. A space-filling drawing based on the X-ray crystal structure of the complex reveals that the steric bulk of the $[\text{Cp}^{4i}]^-$ rings effectively encloses the metal center (Fig. 1).¹²

All the alkaline-earth $(\text{Cp}^{4i})_2\text{Ae}$ metallocenes are high-melting solids (mp of 229-231 °C (Mg), 196-200 °C (Ca), 151-153 °C (Sr), and 149-150 °C (Ba)), and despite their high

molecular weight, are fairly volatile. $(\text{Cp}^{4i})_2\text{Ba}$, for example, sublims at 90 °C and 10^{-2} torr, making it the most volatile known organobarium compound.

2. Monocyclopentadienyl Complexes

Monocyclopentadienyl complexes ($\text{Cp}'\text{AeX}$) are a recently developed class of compounds that combine a single Cp' ring with an anionic group X. Monocyclopentadienyl complexes have types of functionality that are not available from the metallocenes. A common means for their preparation involves the reaction of a metallocene with an Ae dihalide (e.g., eq 2).¹³



Monocyclopentadienyl complexes have not been commonly used as sources of alkaline-earth ions since the examples known before this work were subject to complicating disproportionation reactions (eq 3).^{13,14}



The use of encapsulating cyclopentadienyl groups has significantly improved the handling of these compounds.

B. New Synthetic Studies with Isopropylated Cyclopentadienyl Rings

1. Synthesis of Encapsulated Metallocenes with Altered Physical Properties.

As noted above, the ability of the substituents on a cyclopentadienyl ring to form a "cage" around the metal center is critical to the formation of an encapsulated complex. To determine the extent to which this protective effect would be maintained in metallocenes with less heavily substituted cyclopentadienyl rings, we synthesized triisopropylcyclopentadienyl derivatives $(\text{Cp}^{3i})_2\text{Ae}$ ($\text{Cp}^{3i} = (i\text{-Pr})_3\text{C}_5\text{H}_2$; Ae = Mg–Ba). Unexpectedly, the Ca, Sr, and Ba compounds displayed physical properties completely unlike those of the crystalline $(\text{Cp}^{4i})_2\text{Ae}$ metallocenes.^{15,16} The calcium compound was initially isolated as an oil that slowly crystallized over the course of several weeks, the strontium species

was an oil that resisted crystallization for up to a year, and the freshly sublimed barium compound was a wax that hardened to a powder over several days. In addition, the moderate air-stability of the $(\text{Cp}^{4i})_2\text{Ae}$ compounds was lost in the $(\text{Cp}^{3i})_2\text{Ae}$ derivatives; the latter also could form adducts with ethers without difficulty. Obviously, the removal of a single isopropyl group from the cyclopentadienyl ring dramatically changed not only the physical properties but also the chemical reactivity of the resulting metallocenes.

A single crystal X-ray structure of $(\text{Cp}^{3i})_2\text{Ca}$ found it to be monomeric, and as with $(\text{Cp}^{4i})_2\text{Ca}$, the isopropyl groups in $(\text{Cp}^{3i})_2\text{Ca}$ orient themselves to "encapsulate" the calcium atom (Fig. 2).¹⁶ Unlike $(\text{Cp}^{4i})_2\text{Ca}$, however, the orientations of the six isopropyl groups in $(\text{Cp}^{3i})_2\text{Ca}$ are much more variable (as evidenced by the wider range of angles relative to the ring plane); the "gearing" of the isopropyl substituents found in $(\text{Cp}^{4i})_2\text{Ca}$ is not present in the structure of $(\text{Cp}^{3i})_2\text{Ca}$. This leads to the conclusion that the $[\text{Cp}^{3i}]^-$ rings in $(\text{Cp}^{3i})_2\text{Ca}$ (and other $(\text{Cp}^{3i})_2\text{Ae}$ complexes as well) have several possible geometries in the solid state that are energetically similar. When initially synthesized, $(\text{Cp}^{3i})_2\text{Ca}$ probably is a mixture of complexes with these different orientations, and therefore enters a supercooled state that resists forming a crystalline lattice.

The link between the unusual physical properties of the $(\text{Cp}^{3i})_2\text{Ae}$ metallocenes and the increased flexibility of the $[\text{Cp}^{3i}]^-$ ligand is strengthened by comparisons with the solvated $(\text{Cp}^{3i})_2\text{Ae}(\text{THF})_n$ complexes, all of which are crystalline solids.¹⁵ In these compounds, the isopropyl groups are sterically restricted by interactions with coordinated THF ligands. Such contacts evidently reduce the flexibility in the cyclopentadienyl ligands enough so that crystalline compounds can be obtained.

2. Other potential encapsulating ligands

The cyclohexyl group can be considered a type of "expanded" isopropyl group, and we therefore synthesized metallocenes containing the $(\text{cyclo-C}_6\text{H}_{11})_3\text{C}_5\text{H}_2$ ligand so that they could be compared to the tri- and tetraisopropylcyclopentadienyl derivatives. The

iron complex $[1,2,4-(\text{cyclo-C}_6\text{H}_{11})_3\text{C}_5\text{H}_2]_2\text{Fe}$ was prepared as a prototype, and though it was air-stable, its extreme hydrocarbon solubility made the preparation of solid samples difficult. An X-ray structure of the material was eventually obtained (Fig. 3).¹⁷ The alkaline-earth compounds $[1,2,4-(\text{cyclo-C}_6\text{H}_{11})_3\text{C}_5\text{H}_2]_2(\text{Ca}, \text{Sr}, \text{Ba})$ showed some potential as even more air-stable than the isopropyl derivatives, with the calcium complex lasting for more than 30 min in air.¹⁸ Computer modeling of $[(\text{cyclo-C}_6\text{H}_{11})_3\text{C}_5\text{H}_2]_2\text{Ca}$ suggested that, as with the tetraisopropyl derivatives, the metal center was largely inaccessible in these compounds. Difficulties in preparing pure sample of these materials prevented detailed studies of their properties, however.

Another family of potentially encapsulating ligands that we investigated were those based on polyphenylcyclopentadienyl ligands. Repeated attempts using a variety of approaches failed to produce the decaphenyl-substituted metallocenes, $(\text{Ph}_5\text{C}_5)_2\text{Ae}$, always because of the formation of the persistent neutral radical, $\text{Ph}_5\text{C}_5^\bullet$.¹⁹ The mono-THF adduct of octaphenylbarocene, $(\text{Ph}_4\text{C}_5\text{H})_2\text{Ba}(\text{THF})$ was eventually synthesized and isolated, but unlike all other barocenes (or Group 2 complexes) reported to date, it has only marginal thermal stability. It slowly decomposes in the solid state over several week's time at room temperature, or within hours on attempted sublimation at 120 °C. In this respect, however, it is like other main-group octaphenylmetallocenes (e.g., those with Ge, Sn, and Pb), which are less thermally and kinetically stable than their unsubstituted or decaphenyl analogues; for example, they decompose in minutes in THF at room temperature.²⁰ The reasons for the instability of the octaphenylmetallocenes are not clear; a combination of the Lewis acidity of the metals, open metal coordination sites, and a lack of efficient electron donation from the $\text{C}_5\text{Ph}_4\text{H}$ ligand may be involved.²¹

3. Encapsulation with other metals

If the physical properties associated with encapsulated alkaline-earth metallocenes are largely derived from the geometric properties of the ligands, it should be possible to

induce similar behavior with other metals. This was the case with metals whose radii were similar to those of the alkaline-earths. For example, we prepared the solid deep blue-violet $(\text{Cp}^{4i})_2\text{Sm}$ (radius of $\text{Sm}^{2+} = 1.17 \text{ \AA}$; cf. $\text{Sr}^{2+} = 1.18 \text{ \AA}$ ²²), and obtained its single crystal X-ray structure (Fig. 4). It displays some characteristics of an encapsulated compound, including modest air-stability (minutes) instead of the seconds of $(\text{C}_5\text{Me}_5)_2\text{Sm}$.²³ The analogous $(\text{Cp}^{3i})_2\text{Sm}$ compound is a dark purple oil, physically similar to the strontium compound. Furthermore, the solid $(\text{Cp}^{3i})_2\text{Sm}(\text{THF})$ adduct can be made, which is also similar to the strontium species.²⁴

A series of posttransition metal encapsulated compounds was made using Zn^{2+} , Sn^{2+} , and Pb^{2+} . Those of the Sn^{2+} (ionic radii = 1.18 \AA) have been the most thoroughly investigated, and their properties were found to resemble those of their alkaline-earth counterparts; e.g., $(\text{Cp}^{4i})_2\text{Sn}$ is a highly crystalline solid, air-stable for weeks, whereas $(\text{Cp}^{3i})_2\text{Sn}$ is an air-sensitive oil that does not crystallize even after a year.²⁵ In addition, the crystal structure of $(\text{Cp}^{4i})_2\text{Sn}$ (Fig. 5) reveals it to be isostructural with the bent $(\text{Cp}^{4i})_2\text{Ca}$ compound, including similar interplanar ring angles (152.2° (Sn), 158.9° (Ca)). That the properties of the strontium, samarium, and tin metallocenes should coincide so nearly suggests that the nature of the $\text{M}-\text{Cp}^{\text{ni}}$ bond (highly ionic in Sr and Sm, more covalent in Sn) is not as important as the ability of the $(\text{Cp}^{\text{ni}})_2\text{M}$ units to encapsulate the metals and pack in a regular lattice.

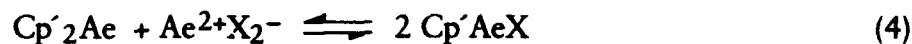
C. Activation of Encapsulated Complexes

1. Ring displacement reactions

Encapsulated metallocenes can be "activated" when one or both rings are displaced so that the metal center is exposed to the solvent and any reagents dissolved in it. Whether this will result in the formation of a monoring species (Cp^iAeX) or a completely inorganic product (i.e., the salt AeXY) will depend to what extent the cyclopentadienyl anions are

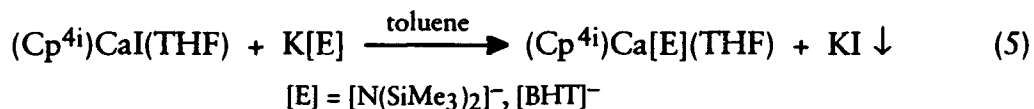
preserved. Reagents that were explored and their possible mode(s) of action are summarized below.

(a) *Ring displacement by nucleophiles.* These can form stable mono(ring) species by taking advantage of the equilibrium between metallocenes and monoring species (eq 4).



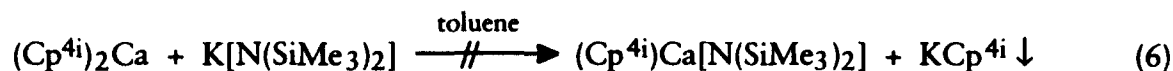
Halides are particularly effective in activating encapsulated metallocenes. For example, the mono[(tetraisopropyl)cyclopentadienyl]calcium halide ($\text{Cp}^{4i}\text{CaI}(\text{THF})_2$) is isolated in high yield (>90%) from the conproportionation of $(\text{Cp}^{4i})_2\text{Ca}$ and CaI_2 in THF. Recrystallization from toluene generates the monosolvated derivative $(\text{Cp}^{4i})\text{CaI}(\text{THF})$, which forms an iodide-bridged dimer, $[(\text{Cp}^{4i})\text{Ca}(\mu\text{-I})(\text{THF})]_2$ (Fig. 6). Unlike the case with mono(ring) complexes prepared from non-encapsulating ligands, no disproportionation of $(\text{Cp}^{4i})\text{CaI}(\text{THF})_{(1 \text{ or } 2)}$ into $(\text{Cp}^{4i})_2\text{Ca}$ and $\text{CaI}_2(\text{THF})_n$ is observed in either THF or aromatic solvents at room temperature. This stability evidently arises from the inability of THF to dissociate completely from the oxophilic calcium center in the mono(tetraisopropylcyclopentadienyl) complexes, which blocks formation of the base-free $(\text{Cp}^{4i})_2\text{Ca}$. Results similar to those with iodide are observed with the chloride and bromide ion.²⁴

$(\text{Cp}^{4i})\text{CaI}(\text{THF})_n$ was found to have distinctive derivative chemistry. It reacts with $\text{K}[\text{N}(\text{SiMe}_3)_2]$ and $\text{K}[\text{BHT}]$ ($\text{HBHT} = \text{HOC}_6\text{H}_2\text{-t-Bu}_2\text{-2,6-Me-4}$) to yield $(\text{Cp}^{4i})\text{Ca}[\text{N}(\text{SiMe}_3)_2](\text{THF})$ and $(\text{Cp}^{4i})\text{Ca}[\text{BHT}](\text{THF})$, respectively, in high yield (eq 5).



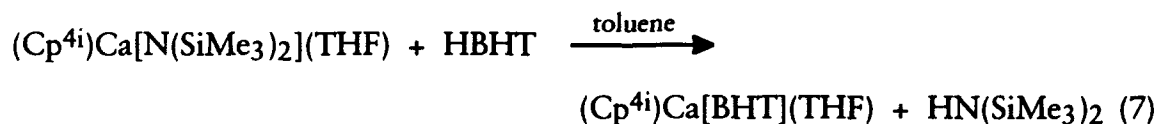
In contrast to the results from the conproportionation reactions with calcium halides, the attempted synthesis of $(\text{Cp}^{4i})\text{Ca}[\text{N}(\text{SiMe}_3)_2](\text{THF})$ by the reaction of $(\text{Cp}^{4i})_2\text{Ca}$ and $\text{Ca}[\text{N}(\text{SiMe}_3)_2]_2$ in THF yielded only ca. 10% of the desired compound. In

addition, $(\text{Cp}^{4i})_2\text{Ca}$ and $\text{K}[\text{N}(\text{SiMe}_3)_2]$ did not react in toluene to form base-free $(\text{Cp}^{4i})\text{Ca}[\text{N}(\text{SiMe}_3)_2]$ and a precipitate of KCp^{4i} , as was expected (eq 6).



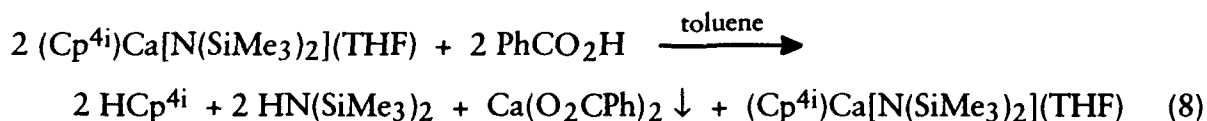
Thus even though it is more basic than any of the halides, the $[\text{N}(\text{SiMe}_3)_2]^-$ anion only reluctantly reacts with $(\text{Cp}^{4i})_2\text{Ca}$. This may be due to its large size, which limits its approach to the metallocene rings.

(b) *Ring displacement by organic/organometallic acids.* Organic /organometallic acids serve as proton sources that could remove a cyclopentadienyl ring by protonation. We used the mono(cyclopentadienyl) complex $(\text{Cp}^{4i})\text{Ca}[\text{N}(\text{SiMe}_3)_2](\text{THF})$ as the test system for estimating the inherent basicity of the $[\text{Cp}^{4i}]^-$ anion; these results are summarized in Table 1. In general, sterically bulky, weak acids ($\text{p}K_a > 10$) selectively protonate only the amide group, even when used in excess; new mono(ring) complexes are the result. A borderline case is provided by HBHT ($\text{p}K_a \approx 10.2$); in a 1:1 reaction in toluene, the following occurs (eq 7).



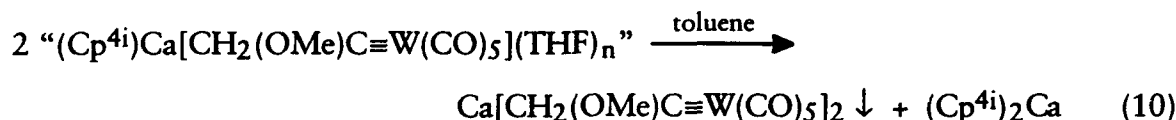
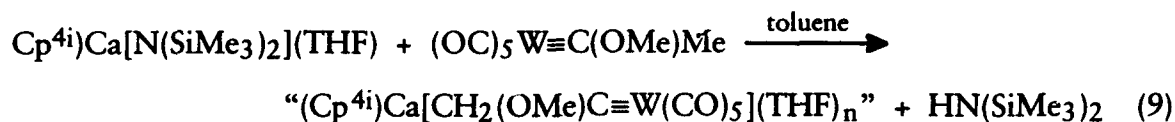
Protonation of the $[\text{Cp}^{4i}]^-$ ligand will occur, however, if excess HBHT is used.

Selective protonation is lost with smaller, stronger acids; e.g., with benzoic acid ($\text{p}K_a = 4.2$), a mixture of products is obtained, even when the ratio of PhCO_2H to $(\text{Cp}^{4i})\text{Ca}[\text{N}(\text{SiMe}_3)_2](\text{THF})$ is 1:1 (eq 8).²⁶



In preliminary work, the acidic organometallic carbyne complex $(\text{OC})_5\text{W}\equiv\text{C}(\text{OMe})\text{Me}$ ($\text{p}K_a \text{ ca. } 12$) was found to protonate the amide ligand, forming a new compound provi-

sionally identified as $(\text{Cp}^{4i})\text{Ca}[\text{CH}_2(\text{OMe})\text{C}\equiv\text{W}(\text{CO})_5](\text{THF})_n$ (eq 9). This heterometallic species is unstable, however, and disproportionates to the encapsulated metallocene $(\text{Cp}^{4i})_2\text{Ca}$ and the calcium salt of the tungsten carbyne anion, $\text{Ca}[\text{CH}_2(\text{OMe})\text{C}\equiv\text{W}(\text{CO})_5]_2$ (eq 10).²⁴



Loss of THF from the calcium center must occur at some point in order for formation of $(\text{Cp}^{4i})_2\text{Ca}$ to occur.

2. Improved volatility and stability of encapsulated complexes

We have found the volatility of $(\text{Cp}^{4i})_2\text{Ba}$ to compare favorably with $\text{Ba}(\text{FOD})_2$ (subl. 210°C , 0.2 torr) and $\text{Ba}(\text{TMHD})_2$ (subl. 225°C , 0.05 torr), compounds that have found substantial use in chemical vapor deposition (CVD) applications.^{27,28} Preliminary work has shown some promise with $(\text{Cp}^{4i})_2\text{Ba}$ as a precursor to barium oxide under CVD conditions, although, as is common with ligands containing unsaturated carbon atoms, carbide contamination of the oxide remains a problem.²⁹

Figure 7 presents the sublimation temperatures and corresponding molecular weights for a variety of barocenes. The sublimation temperatures drop on going from the polymeric Cp_2Ba (450°C) to the monomeric $(\text{Cp}^{4i})_2\text{Ba}$ (90°C), though there is more than a two-fold rise in molecular weight (from 270 to 600 g/mol). This data suggests that the greatest impediment to producing metallocenes of high volatility is the inability of conventionally sized ligands to block the intermolecular forces that cause oligomerized or polymerized structures. The difference in sublimation temperatures for $(\text{Cp}^{3i})_2\text{Ba}$ ($120^\circ\text{C}/10^{-6}$

torr) and $(\text{Cp}^{4i})_2\text{Ba}$ ($90\text{ }^\circ\text{C}/10^{-2}$ torr) suggests that rigorously complete encapsulation is necessary before the maximum increases in volatility can be expected.

3. Thermal Behavior of Heteroleptic Complexes

Only recently we have discovered that some mono(ring) complexes containing an encapsulating cyclopentadienyl ring have thermal properties that are substantially different from those found in compounds with smaller Cp rings. For example, the base-free complex $[(\text{Cp}^{4i})\text{CaI}]_n$ was prepared from $(\text{Cp}^{4i})\text{CaI}(\text{THF})_n$ by heating under vacuum. It is soluble in toluene although insoluble in hexane and begins to convert to a mixture of $(\text{Cp}^{4i})_2\text{Ca}$ and CaI_2 at $215\text{ }^\circ\text{C}$. This suggests that it could be coated on substrates by solution-based methods, and thin layers of CaI_2 would be left on heating only slightly above the sublimation temperature of $(\text{Cp}^{4i})_2\text{Ca}$ itself ($190\text{ }^\circ\text{C}/10^{-6}$ torr).³⁰ It should be noted that, in contrast, $[(\text{C}_5\text{Me}_5)\text{CaI}]_n$ is completely insoluble in hydrocarbons, and displays no evidence of volatility or decomposition at temperatures up to $240\text{ }^\circ\text{C}$ under high vacuum. The smaller size of the C_5Me_5 ring evidently allows the $[(\text{C}_5\text{Me}_5)\text{CaI}]_n$ complex to polymerize extensively.

As another example, $(\text{Cp}^{4i})\text{Ca}[\text{N}(\text{SiMe}_3)_2](\text{THF})$ can be sublimed readily at $120\text{ }^\circ\text{C}$ and 10^{-6} torr to give a glassy or waxy material in ca. 60% yield. In contrast, the corresponding bis(ligand) calcium complexes $(\text{Cp}^{4i})_2\text{Ca}$ and $\text{Ca}[\text{N}(\text{SiMe}_3)_2]_2$ are not as volatile: $(\text{Cp}^{4i})_2\text{Ca}$ sublimes at $190\text{ }^\circ\text{C}$ and 10^{-6} torr,¹² and $\text{Ca}[\text{N}(\text{SiMe}_3)_2]_2(\text{DME})_2$ has been reported to sublime with much decomposition at $150\text{ }^\circ\text{C}$ under high vacuum.³¹ In this case, the larger $[\text{Cp}^{4i}]^-$ ligand in $(\text{Cp}^{4i})\text{Ca}[\text{N}(\text{SiMe}_3)_2](\text{THF})$ confers added stability compared to the bis(amido) complex, and the reduced mass of the $[\text{N}(\text{SiMe}_3)_2]^-$ ligand in $(\text{Cp}^{4i})\text{Ca}[\text{N}(\text{SiMe}_3)_2](\text{THF})$ increases its volatility relative to the metallocene.

These results suggest that a type of "ligand synergism" exists in heavy alkaline-earth complexes that has until now remained largely unexplored. Heteroleptic complexes containing an encapsulating cyclopentadienyl ring provide a degree of freedom in designing

complexes with desirable physical characteristics that is not available to the symmetrical bis-ligand compounds.

D. Summary of Key Results

1. Encapsulation of metallocenes is associated with distinctive changes in their physical properties (e.g., reduced sensitivity to oxygen, enhanced volatility); it is generally independent of the nature of the metal-ring bonding. The effects of encapsulating ligands are not confined to alkaline-earth materials, but can be induced in other main group species (Sn, Pb) and in lanthanide compounds (Sm).

2. The physical properties of the metallocenes are highly sensitive to the degree of encapsulation. The highest levels of volatility require complete encapsulation of the metal center, and blocking intermolecular forces is evidently more important than minimizing molecular weights. Melting points are also sensitive to the geometry of the encapsulating ligands; flexible rings reduce the ability of complexes to pack into regular lattices, and oils and waxes will be formed.

3. A high degree of kinetic control can be built into organoalkaline-earth compounds through careful ligand choice. With appropriate nucleophiles, a ring can be displaced from an encapsulated metallocene, exposing the metal center and activating the complex. Disproportionation of the resulting mono(ring) complexes $\text{Cp}'\text{M}[\text{E}]$ into the symmetrical $\text{Cp}'_2\text{M}$ and $\text{M}[\text{E}]_2$ species can be blocked, and selective ligand removal by protonation is possible. "Ligand synergism" in mono(ring) complexes can enhance the chemical and thermal properties over those of the parent symmetrical species.

III. Publications Citing ARO Support

1. D. J. Burkey, R. A. Williams, and T. P. Hanusa, "Encapsulated Alkaline-earth Metallocenes. 2. Triisopropylcyclopentadienyl Systems, $[(C_3H_7)_3C_5H_2]_2Ae(THF)_n$ ($Ae = Ca, Sr, Ba; n = 0 - 2$) and the Crystal Structure of $[(C_3H_7)_3C_5H_2]_2Ba(THF)_2$," *Organometallics*, 1993, 12, 1331-1337.
2. T. P. Hanusa, "Ligand Influences on Structure and Reactivity in Organoalkaline-earth Chemistry," *Chem. Rev.*, 1993, 93, 1023-1036.
3. D. J. Burkey, T. P. Hanusa, and J. C. Huffman, "Encapsulated Alkaline-earth Metallocenes. 3. Structural Influences on Phase Transformations in Alkaline-earth Complexes," *Adv. Mater. Opt. Electron.*, 1994, 4, 1-8.
4. P. S. Tanner and T. P. Hanusa, "Encapsulated Alkaline-earth Metallocenes. 4. Thermal Instability in Tetraphenylcyclopentadienyl Barium Complexes," *Polyhedron*, in press.
5. J. A. Burman, M. L. Hays, D. J. Burkey, P. S. Tanner, and T. P. Hanusa, "Synthesis and Structural Characterization of Hexa(cyclohexyl)ferrocene, $[1,2,4-(C_6H_{11})_3C_5H_2]_2Fe$," *J. Organomet. Chem.*, in press.
6. D. J. Burkey, E. K. Alexander and T. P. Hanusa, "Encapsulated Alkaline-Earth Metallocenes. 5. Kinetic Stabilization of Mono[(tetraisopropyl)cyclopentadienyl]calcium Complexes," *Organometallics*, in press.
7. D. J. Burkey and T. P. Hanusa, "Structural Lessons from Main-Group Metallocenes," in preparation.
8. D. J. Burkey and T. P. Hanusa, "Synthesis and Characterization of the Encapsulated Tin Metallocenes $[(C_3H_7)_3C_5H_2]_2Sn$ and $[(C_3H_7)_4C_5H]_2Sn$," in preparation.

IV. Participating Scientific Personnel

1. Mr. S. Craig Sockwell (Ph.D., Aug 1991)
2. Mr. Kris F. Tesh (Ph.D., Dec 1991)
3. Ms. Pamela S. Tanner (No degree)

V. Inventions

There were no inventions developed under ARO 28402CH.

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VII. Figures and Tables

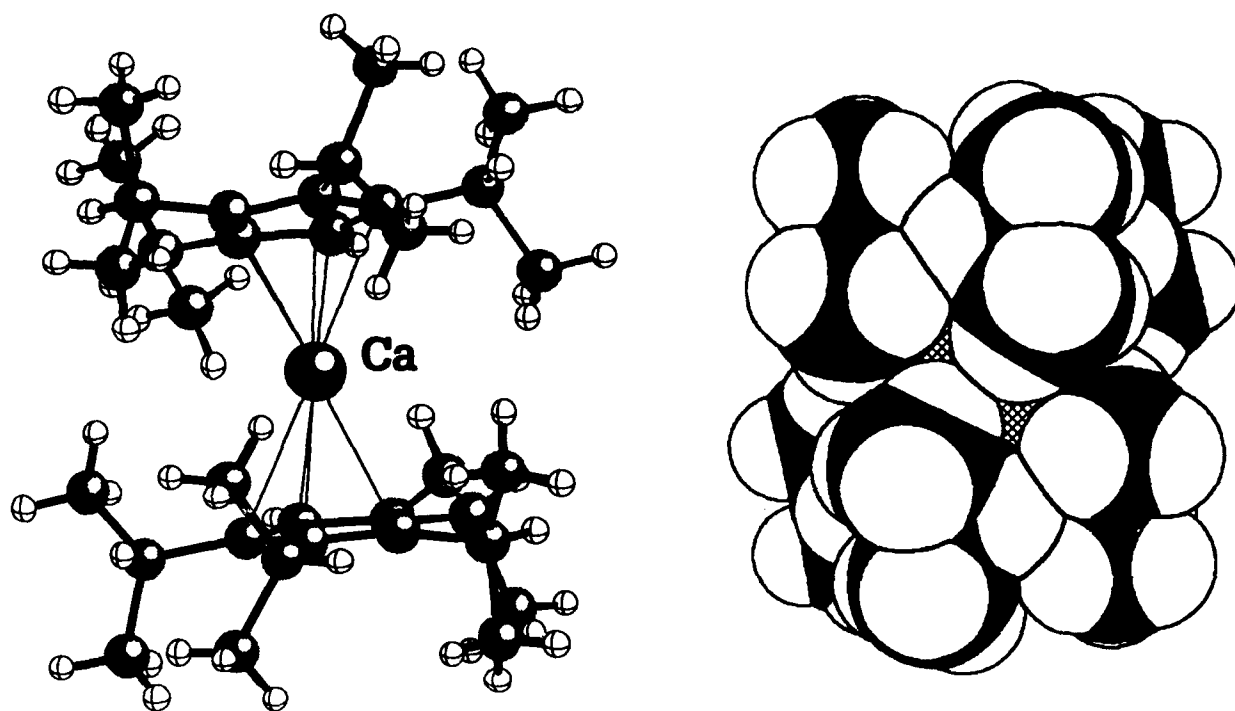


Fig. 1 Ball-and-stick drawing of $(\text{Cp}^{4i})_2\text{Ca}$ on the left; on the right, a space-filling view of the same complex, indicating the near-total encapsulation of the calcium (crosshatched area).

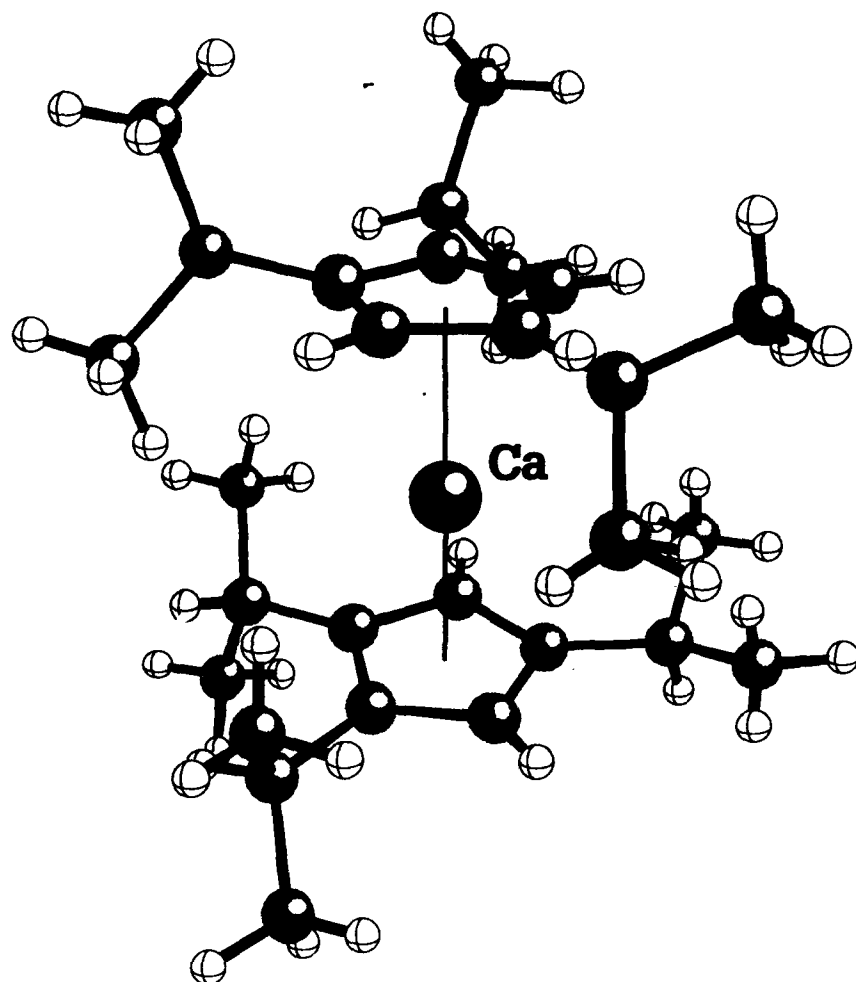


Fig. 2 Ball-and-stick drawing of $(\text{Cp}^{3i})_2\text{Ca}$, as determined by X-ray diffraction. Notice the variety of isopropyl group orientations around the ring; this contributes to the ease with which the compound supercools.

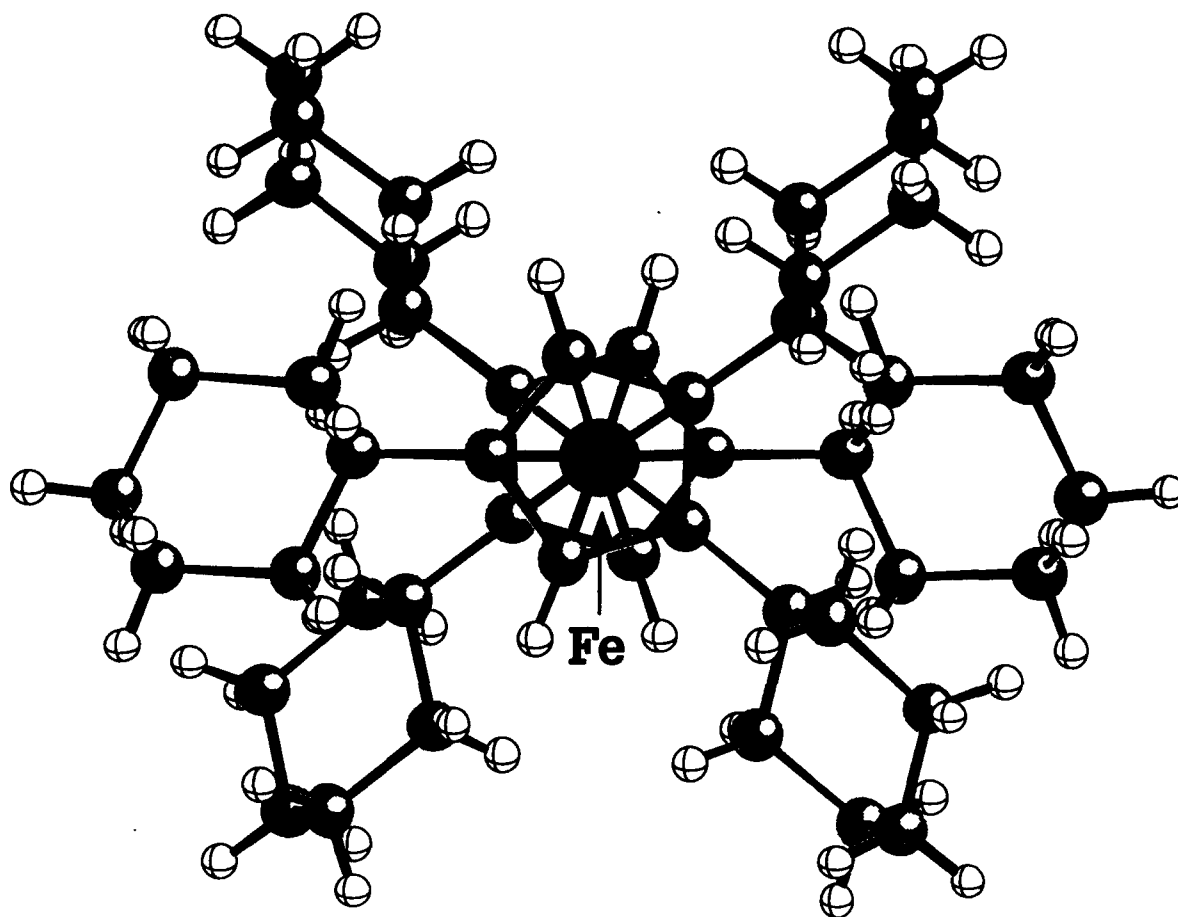


Fig. 3. Top-side ball-and-stick drawing of $[1,2,4-(\text{C}_6\text{H}_{11})_3\text{C}_5\text{H}_2]_2\text{Fe}$, illustrating the way the cyclohexyl groups encapsulate the iron.

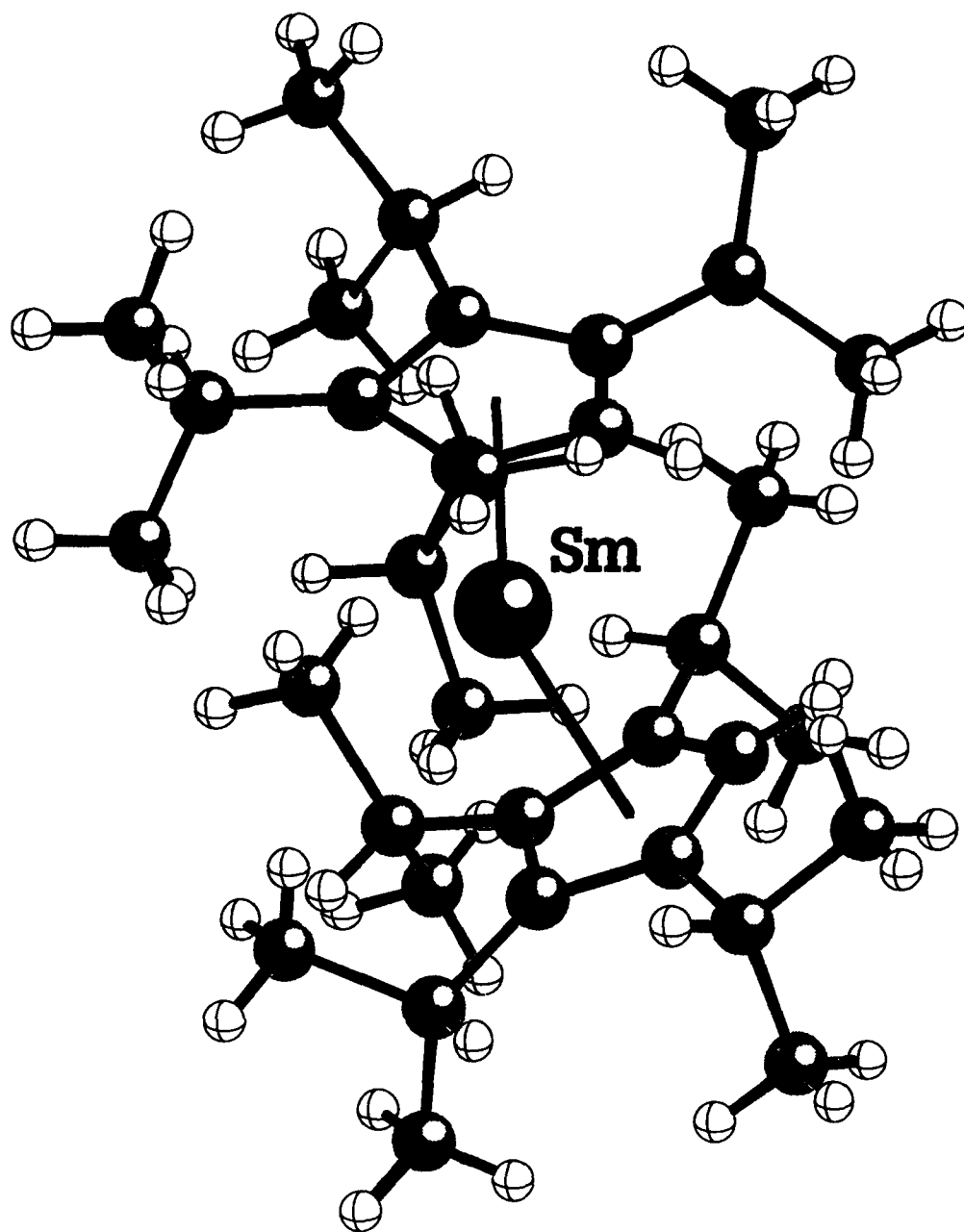


Fig. 4 Ball-and-stick drawing of $(\text{Cp}^{4i})_2\text{Sm}$. The compound is isostructural with the calcium and tin metallocenes.

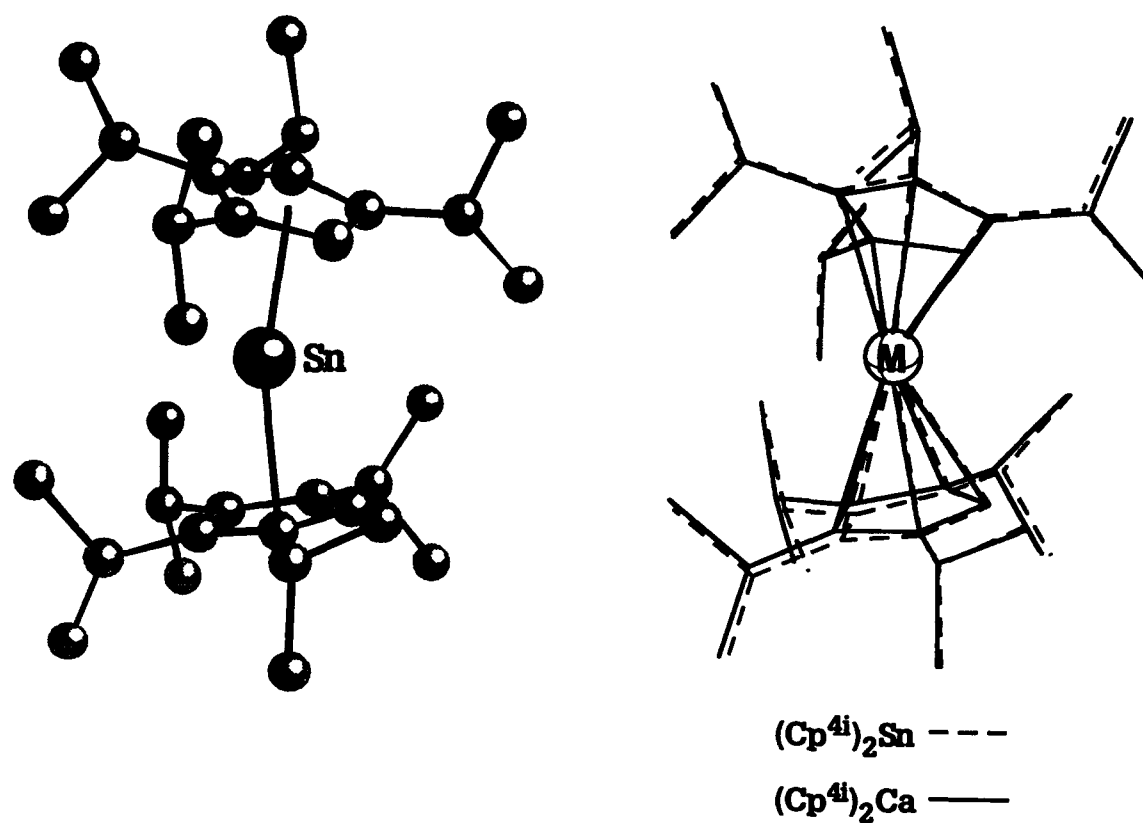


Fig. 5. Ball-and-stick drawing of $(\text{Cp}^{4i})_2\text{Sn}$ (left). On the right, a superposition of the solid state structures of $(\text{Cp}^{4i})_2\text{Ca}$ and $(\text{Cp}^{4i})_2\text{Sn}$; despite the differences in metal-ligand bonding, the two encapsulated metallocenes are isostructural.

Fig. 6. Ball-and-stick drawing of the solid state structure of $\{(\text{Cp}^{4\text{i}})\text{Ca}(\mu\text{-I})(\text{THF})\}_2$, as determined by X-ray diffraction.

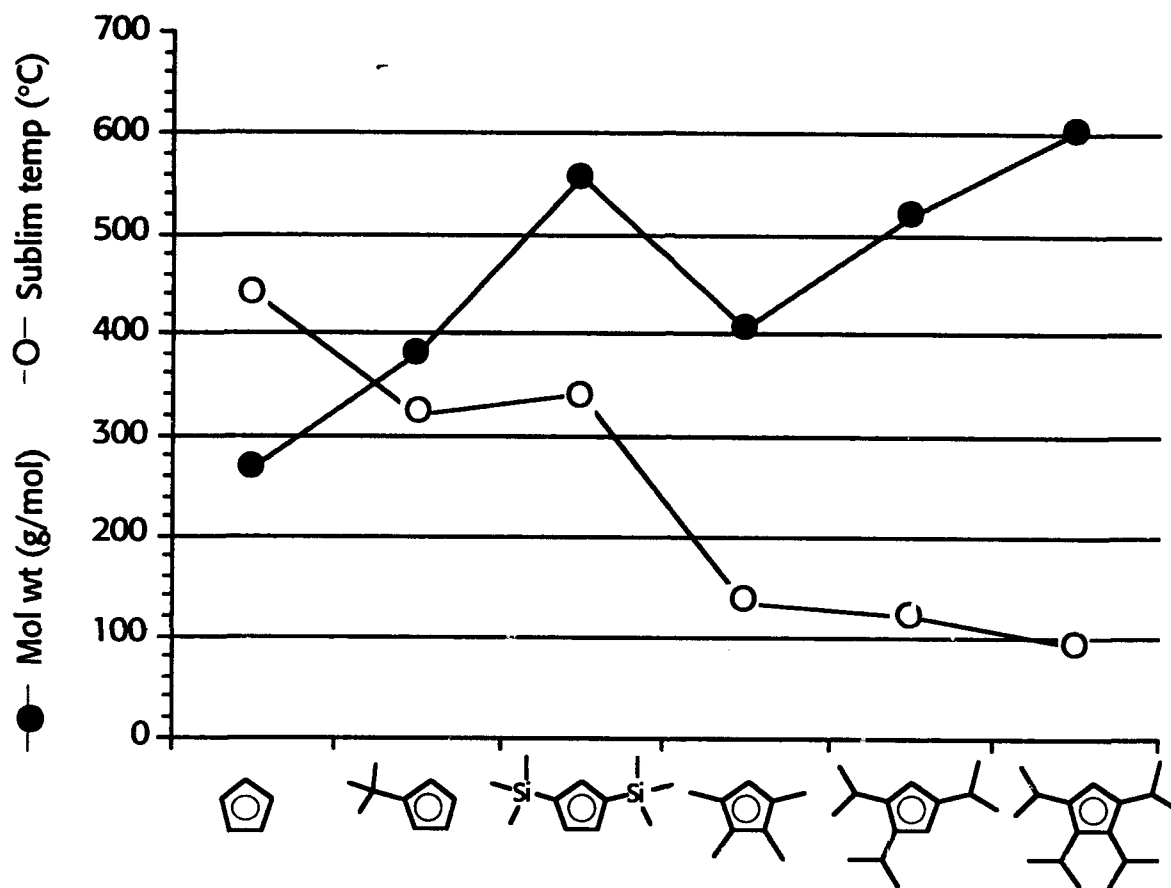


Fig. 7 Sublimation temperatures of base-free barocenes as a function of molecular weight and increasing steric bulk of the cyclopentadienyl ligands. Note that an encapsulated metallocene, such as $(\text{Cp}^{3i})_2\text{Ba}$, has a sublimation temperature that is 220 °C (65%) lower than that of non-encapsulated $[(\text{Me}_3\text{Si})_2\text{C}_5\text{H}_3]_2\text{Ba}$, though the molecular weights differ by only 7% (520 and 556 g/mol, respectively).

Table 1. Products from the reaction of $(\text{Cp}^{4i})\text{Ca}[\text{N}(\text{SiMe}_3)_2](\text{THF})$

| Acid | $\text{p}K_{\text{a}}$ | Metal-containing Product(s) |
|--|------------------------|---|
| $\text{HC}\equiv\text{CSiMe}_3$ | <i>ca.</i> 19 | $(\text{Cp}^{4i})\text{CaC}\equiv\text{CSiMe}_3(\text{THF})$ |
| $\text{HC}\equiv\text{CSi}(i\text{-Pr})_3$ | <i>ca.</i> 19 | $(\text{Cp}^{4i})\text{CaC}\equiv\text{CSi}(i\text{-Pr})_3(\text{THF})$ |
| $\text{HC}\equiv\text{CPh}$ | 18.5 | $(\text{Cp}^{4i})\text{CaC}\equiv\text{CPh}(\text{THF})$ |
| BHT | 10.2 | $(\text{Cp}^{4i})\text{Ca}[\text{BHT}](\text{THF})$ |
| Benzoic acid | 4.2 | $\text{Ca}(\text{O}_2\text{CPh})_2$, $(\text{Cp}^{4i})\text{Ca}[\text{N}(\text{SiMe}_3)_2](\text{THF})$ |